

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

1030,888



PATENT SPECIFICATION

NO DRAWINGS

1030,888

Date of Application and filing Complete Specification: Nov. 3, 1964.

No. 44820/64.

Application made in United States of America (No. 328,164) on Dec. 5, 1963.

Complete Specification Published: May 25, 1966.

© Crown Copyright 1966.

Index at acceptance:—C3 T(6D1A, 6D1B, 6D2, 6D4, 6D5, 6D8, 6D10, 6F1, 6F2, 6G7F, 6G7H);
C3 S(1C, 1D, 3A, 3B, 3D, 4, 6, 7A, 7B, 7D, 8, 9); D1 P(A6, B5A,
C2A12A9, C2C2, C2C3, C2C5, C2C6, C2C7, C2C8, C2C9, C2C10,
C2C17, C2C18, C2C1X)

Int. Cl.:—C 08 g 31/00 // C 07 f, D 06 m

COMPLETE SPECIFICATION

Silanes and Siloxanes

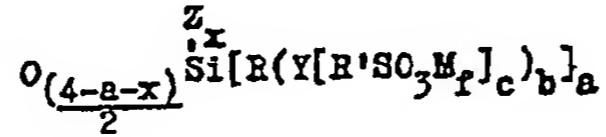
We, Dow CORNING CORPORATION, of Midland, Michigan, United States of America, a corporation organised under the laws of the State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new, sulphopropylated organo-functional silanes and siloxanes which are useful as detergents, ion exchange resins, wetting agents, antistat agents for synthetic fibres, and polymerisation catalysts for siloxanes.

The silanes of this invention are of the general formula $Z_x Si[R(Y[R'SO_3M_f]_c)_b]_a$, where R is a divalent or trivalent hydrocarbon, halohydrocarbon, or hydrocarbon ether radical, there being not more than two Y

groups on any one carbon atom, Y is a $\begin{array}{c} O \\ || \\ C \\ || \\ R''_a \end{array}$, $\begin{array}{c} R''_a \\ | \\ O \\ || \\ C \\ | \\ R''_a \end{array}$, $\begin{array}{c} R''_a \\ | \\ O \\ || \\ C \\ | \\ R''_a \end{array}$, $\begin{array}{c} R''_a \\ | \\ O \\ || \\ C \\ | \\ R''_a \end{array}$, $\begin{array}{c} R''_a \\ | \\ O \\ || \\ C \\ | \\ R''_a \end{array}$, radical where each R'' is independently selected from the hydrogen atom and aliphatic hydrocarbon radicals containing from 1 to 6 inclusive carbon atoms, Q is an alkylene radical containing 2 to 4 inclusive carbon atoms that separates the two N groups by at least two carbon atoms, d is 0 or 1, R' is an alkylene radical that separates Y and SO₃, by three carbon atoms, M is a hydrogen atom, an ammonium radical or a metal atom, c is 1, 2 or 3; b is 1 or 2, a is 1 or 2, and f is the reciprocal of the valency of M, Z is a hydrogen atom or monovalent hydrocarbon, alkoxy, beta-alkoxyalkoxy, phenoxy, acyloxy, or hydrocarbyl-substituted isocyanoxy radical, and e is 2 or 3, the sum of e and a being 4.

The siloxanes of this invention contain at least one unit of the general formula



where x is 0, 1 or 2, and the other symbols are as defined above; any other units in the siloxane being of the general formula $A_g SiO_{\frac{(4-a-x)}{2}}$, where g is 0, 1, 2 or 3, and

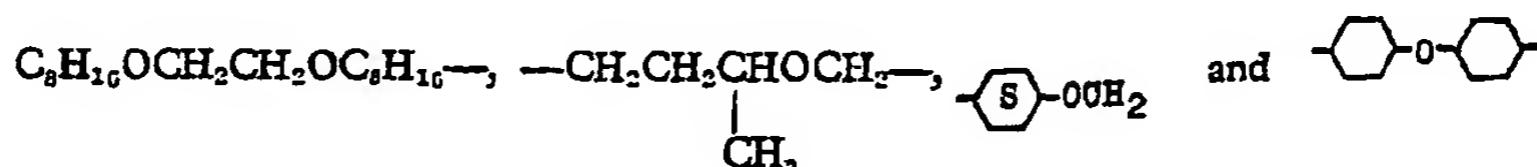
A is a hydrogen atom, monovalent hydrocarbon or halohydrocarbon radical, alkoxy, beta-alkoxyalkoxy, acyloxy, phenoxy, hydrocarbyl-substituted isocyanoxy, or hydroxy radical.

R may be any divalent hydrocarbon radical such as methylene, octadecylene, isobutylene, allylene, butadiylene, cyclohexylene, phenylene, tolylene, 1-phenyl-ethylene; any divalent halohydrocarbon radical such as chlorobutylene, decafluorooctadecylene, 3-bromopropylene, 3-chloroallylene, tetrafluorophenylene; and any

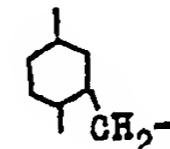
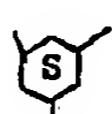
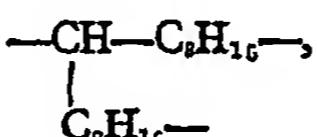
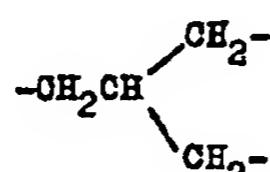
[Price]

2

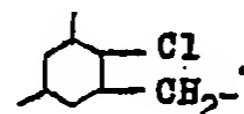
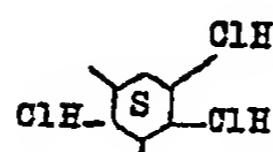
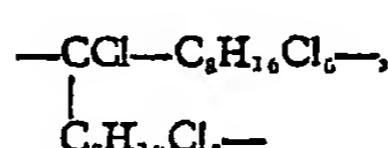
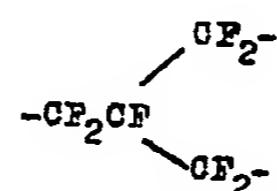
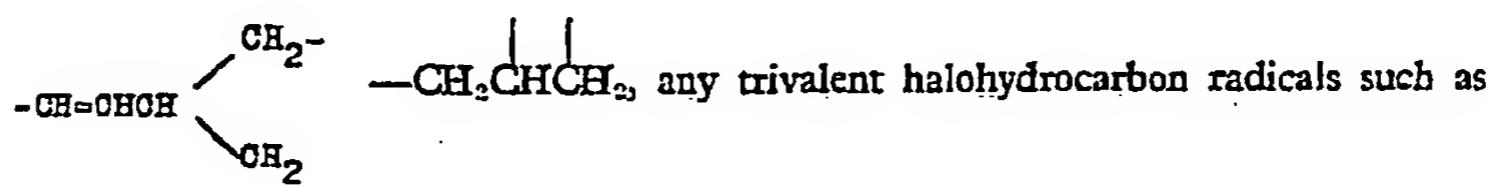
1,030,888

divalent hydrocarbon ether radical such as $-\text{CH}_2\text{CH}_2\text{OCH}_2-$,

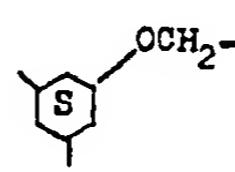
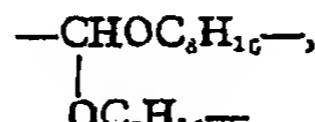
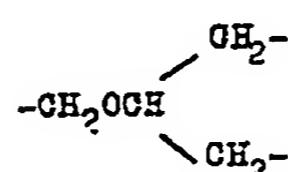
R can also be any trivalent hydrocarbon radical such as



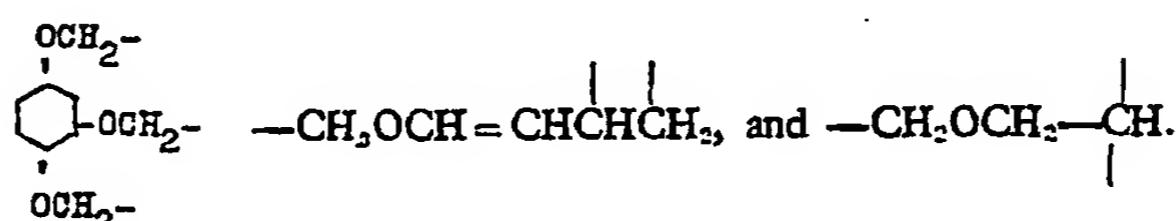
5



or any trivalent hydrocarbon ether radical such as



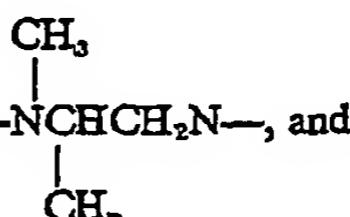
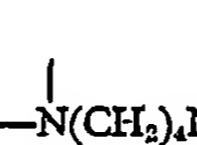
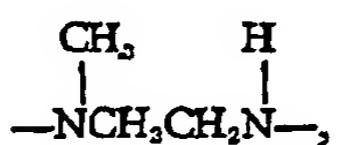
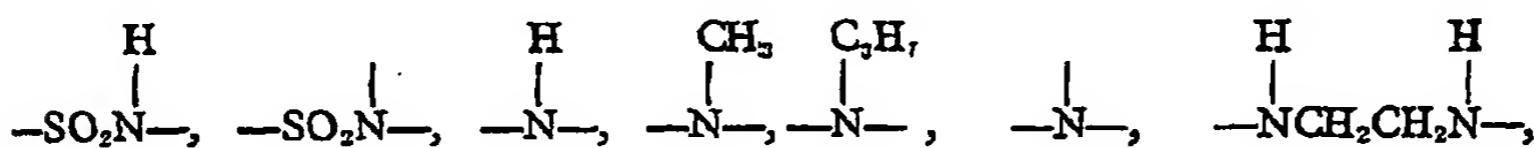
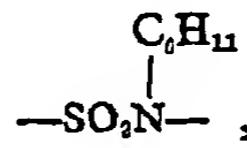
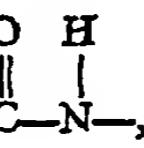
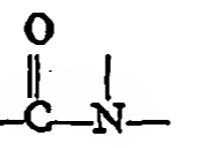
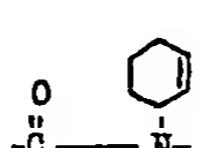
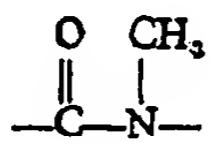
10



R'' can be a hydrogen atom or any monovalent aliphatic hydrocarbon radical containing 1 to 6 inclusive carbon atoms such as methyl, isopropyl, hexyl and cyclohexyl.

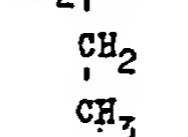
Q can be any divalent alkylene radical containing 2 to 4 inclusive carbon atoms, that separates the two N groups by at least 2 carbon atoms, such as ethylene, propylene, butylene, and isopropylene. 15

Y can be exemplified by $\text{C}=\text{O}-\text{O}-$, $-\text{S}-$, $-\text{O}-$, $-\text{SO}_3-$, $-\text{C}(=\text{O})-\text{N}-$,



5

5



but is preferably $-\text{NH}.\text{CH}_2\text{CH}_2.\text{NH}-$ or $-\text{N}-$

R' can be any alkylene radical that separates Y and SO_3- by three carbon atoms such as propylene, isobutylene, 2-ethylpropylene, 1,2,3-trimethylpropylene, 2,2-



dimethylpropylene and $-\text{CH}_2\text{CH}(\text{CH}_3)-$.

10

M can be a hydrogen atom, an ammonium radical, or any metal atom such as sodium, potassium, calcium, magnesium, aluminium, iron (ferric or ferrous), manganese and copper.

10

15

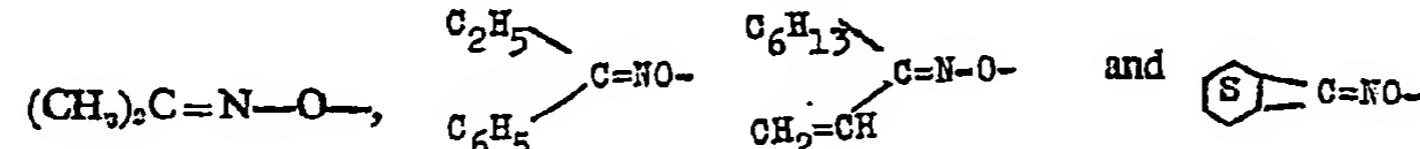
Z can be a hydrogen atom; any monovalent hydrocarbon or halohydrocarbon radical such as methyl, chloromethyl, octadecyl, decabromoocatadecyl, 3,3,3-trifluoropropyl, vinyl, cyclohexyl, perchlorocyclohexyl, phenyl, iodophenyl, tolyl and isobutyl; any alkoxy radical such as methoxy, isopropoxy, decoxy and ethoxy; any beta-alkoxy-alkoxy radical such as $\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}-$, $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{O}$ and $\text{C}_6\text{H}_{13}\text{OCHCH}_2\text{O}-$; any acyloxy radical such as acetate, propionate, isopropionate,

15



isobutyrate and decanoate; phenoxy; any hydrocarbyl-substituted isocyanoxy such as

20



20

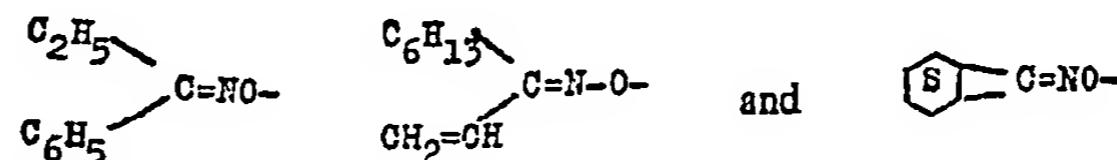
25

A can be a hydrogen atom; any monovalent hydrocarbon or halohydrocarbon radical such as methyl, chloromethyl, octadecyl, decabromoocatadecyl, 3,3,3-trifluoropropyl, vinyl, cyclohexyl, perchlorocyclohexyl, phenyl, iodophenyl, tolyl, and isobutyl; any alkoxy radical such as methoxy, isopropoxy, decoxy, and ethoxy; any beta-alkoxyalkoxy radical such as $\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}-$, $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{O}$ and $\text{C}_6\text{H}_{13}\text{OCHCH}_2\text{O}-$; any acyloxy radical such as acetate, propionate, isopropionate,

25



isobutyrate, decanoate etc.; phenoxy; any hydrocarbyl-substituted isocyanoxy such as $(CH_3)_2C=N-O-$,

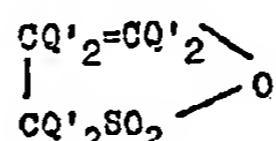


and hydroxy radicals.

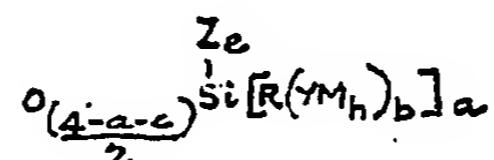
5 Infra-red studies indicate that when Y is an amino group, internal and polymeric salts can be formed between the amino and sulphonate groups.

5

The compounds of this invention can be made by reacting a propane sultone of the general formula



10 with compounds of the general formula $Z_eSi[-R(YM_h)_b]_a$, or with siloxane-containing units of the formula



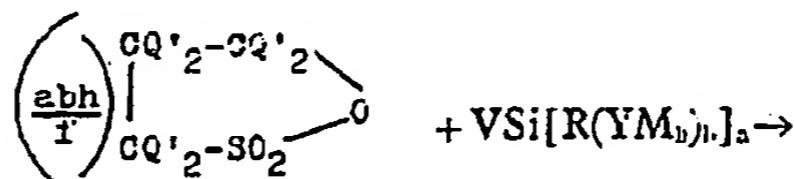
10

where h is the valency of Y divided by the valency of M, each Q' is a hydrogen atom or an alkyl radical, and the other symbols are identified above.

15 It should be noted that h can be fractional, i.e., that there may be more than one Y group per M group. For example, if Y is $COO-$ (monovalent) and M is calcium (divalent), then h is one-half; in other words, there are two Y groups attached to each calcium atom. But, if Y is $-N=$ (divalent) and M is H (monovalent), then h is 2. In that case, there are two M groups per Y group.

15

20 The generic reaction for making the compounds of this invention is



20

$VSi[R(Y[R'SO_2M]_c)_b]_a$ where V symbolises the rest of the molecule, consisting of Z and/or siloxane groups; the product being a compound of this invention.

For example, if we wish to react 3-hydroxyl-1-propane sulphonate sultone

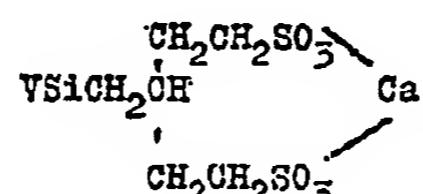


25 with $VSiCH_2CH_2COONa$ we can see that a equals 1, b equals 1, h equals $1/1$ or 1, and f equals $1/1$. Therefore, $\frac{abh}{f}$ equals 1, i.e., one mole of sultone reacts with one

25

mole of silyl group.

However, if we use



30 instead of the above silyl compound, then a equals 1, b equals 2, h equals $1/2$, and f equals $1/2$. $\frac{abh}{f}$ therefore, equals 2, meaning that two moles of sultone can react with one mole of silyl group.

30

h and *f* are included in the expression abh/f to account for the case where Y and M are of unequal valency. For example, if we replace the above silyl compound with $VSi(CH_2CH_2CHNCH_2CH_2NH_2)_2$, then *a* equals 2, *b* equals 1, *h* equals 3/1,

and *f* equals 1/1. $\frac{abh}{f}$, therefore, equals 6; i.e. up to six moles of sultone will react

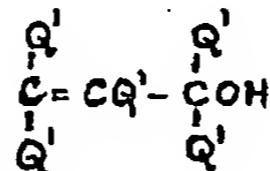
5 with each mole of the above silyl compound.

This reaction can be carried out anywhere in the range of about 20° to about 150° C. A common solvent such as methanol or benzene is added to the reaction mixture along with the reactants. Heating of the reaction mixture should be with caution, for some of the reactions are exothermic, e.g. reactions where a primary amine is involved.

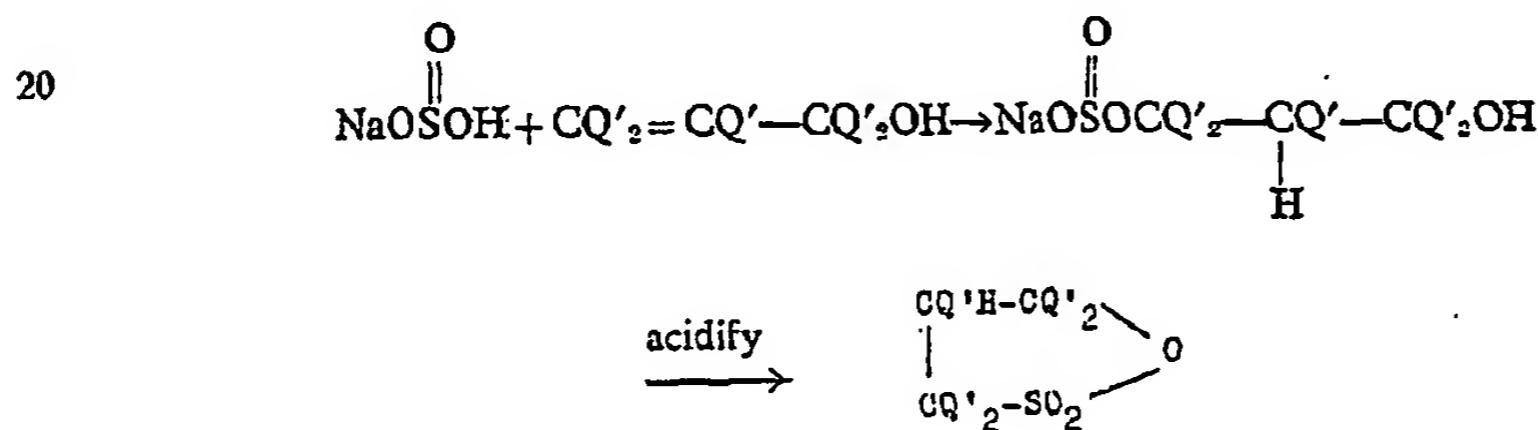
10 If the product is not an insoluble salt, as many of the metal salts are, an alkaline catalyst will often push the equilibrium of the reaction toward the product end, enhancing the yield.

15 The reactants can all be prepared by well-known processes; many of them are sold commercially.

15 The sultones shown above can be prepared by reacting sodium bisulphite with a compound of the following general formula:



where Q' is defined above. The reaction is as follows:



20 Numerous other methods for preparing sultones are known to the art. For example, German Specification No. 1,107,220 discloses the method of heating gamma or delta-halosulphonic acid salts of sodium or ammonium in a vacuum, to obtain a sultone plus the halide of sodium or ammonium. German Specification No. 902,615 discloses the method of making sultones from aliphatic ether monosulphonic acids. A number of other methods can also be found in the literature.

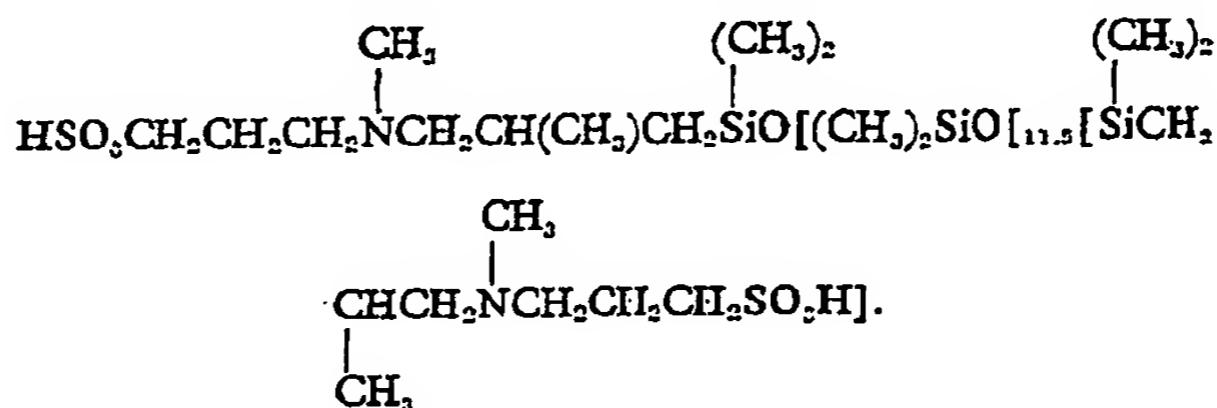
25 The following examples illustrate the invention.

EXAMPLE 1.

30 A flask was charged with 115.8 g. of



35 and 230 ml. of benzene. The mixture was refluxed for two hours to drive moisture from the system. The mixture was cooled to 27° C. and 24.4 g. of 3-hydroxy-1-propane sulphonic acid sultone was added over a period of one minute. The reaction was somewhat exothermic. The reaction product was stripped to 140° C. at 2.0 mm. pressure to remove the benzene. The residue had the following structure:



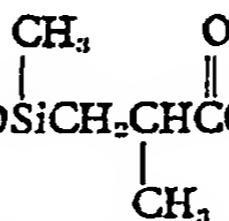
EXAMPLE 2.

5 In a flask was placed 111.2 g. of $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NH}_2$ and 230 ml. of benzene. This was refluxed for one hour at $85^\circ - 86^\circ \text{ C.}$ to remove moisture. The reaction mixture was cooled to 31° C. and 61.1 g. of 3-hydroxy-1-propane sulphonic acid sultone was added. Within two minutes the reaction temperature had increased to 48° C.

10 The product was stripped to 144° C. at 18 mm. pressure to remove the solvent. A product of the following structure was obtained:



EXAMPLE 3.



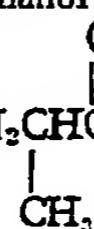
15 In a flask was placed 13.6 g. of $(\text{OSiCH}_2\text{CHCOH}_n)_n$, 5.5 g. of sodium

methoxide, and 77.7 g. of methanol. An exothermic reaction resulted.

To this mixture was added 12.2 g. of 3-hydroxy-1-propane sulphonic acid sultone, and the reaction mixture was refluxed at 65.5° C. for two hours.

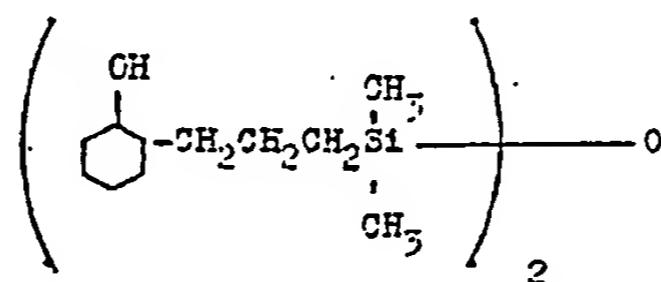
The methanol was evaporated from the solution, and the product isolated. 25.8

g. of $(\text{OSiCH}_2\text{CHCO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na})_n$ was obtained as an amorphous solid.



EXAMPLE 4.

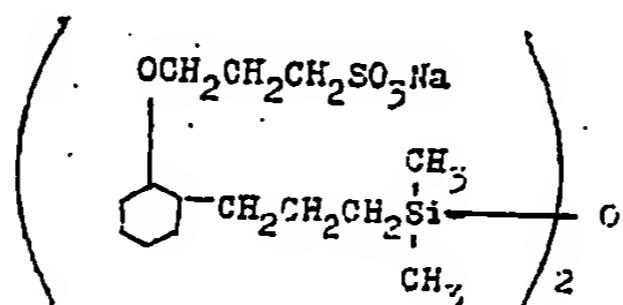
20 In a 500 ml. flask was placed 20.1 g. of



25 77.7 g. of methanol, and 5.5 g. of sodium methoxide. The mixture was warmed in a range of 26.5° to 32° C. while an exothermic reaction took place, completely reacting the sodium methoxide. Then 12.4 g. of 3-hydroxy-1-propane sulphonic acid sultone was added, and the reaction mixture was refluxed at 66.5° C. for 2 hours.

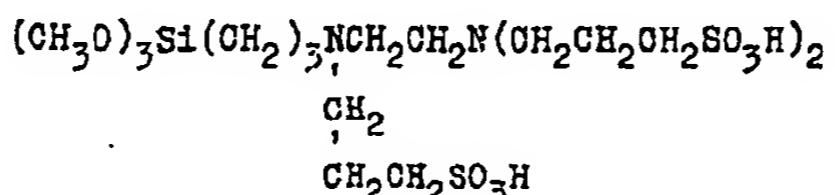
A pink solid product was obtained on removing the methanol.

The product was



EXAMPLE 5.

EXAMPLE 5. In a 500 ml. flask was placed 27.8 g. of $(CH_3O)_3Si(CH_2)_2$, $NHCH_2CH_2NH_2$, and 45.9 g. of 3-hydroxy-1-propane sulphonic acid sultone was added over a 30 second period. The temperature of the reaction mixture rose from 28° C. to 94° C. without outside heating. On cooling, a hydroscopic solid was isolated with a formula:



EXAMPLE 6.

EXAMPLE 5.
In a 500 ml. flask was placed 19.6 g. of $(CH_3O)_2SiCH_2CH_2SH$, 100 ml. of methanol, and 5.49 g. of sodium methoxide. The temperature of the reaction mixture rose slightly, indicating the formation of $(CH_3O)_2SiCH_2CH_2SNa$.

EXAMPLE 7.

A. 2 G. of the siloxane product of Example 1. were dissolved in 98 g. of CH₃OH. A 12.7 cm. by 17.8 cm. piece of nylon fabric was dipped in this solution and dried in the air.

20 B. 2 G. of $(CH_3O)_3SiCH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2CH_2SO_3H$ were dissolved in 98 g. of CH_3OH . A 12.7 cm. by 17.8 cm. piece of nylon fabric was 20 dipped in this solution and dried in the air.

25 C. A 12.7 cm. by 17.8 cm. piece of nylon fabric was not treated. The three nylon squares were each rubbed in one direction several times with a glass rod. The squares were placed over but not in contact with cigarette ashes. Ashes were found to be picked up only by Sample C.

WHAT WE CLAIM IS:—

1. Compounds of the general formula $Z_2Si[-R(-Y[-R'SO_3M_1]_2)_2]_2$, where R is a divalent or trivalent hydrocarbon, halohydrocarbon, or hydrocarbon ether radical, there being not more than 2 Y groups on one carbon atom,

30 Y is a C=O —, —S—, —O—, C=O-N(R'')_a —, SO_3 —, $\text{SO}_2\text{N(R'')}_a$ —, N(R'')_a —, or
 $\text{N(R'')}_a-\text{Q}-\text{N(R'')}_a$ radical where each

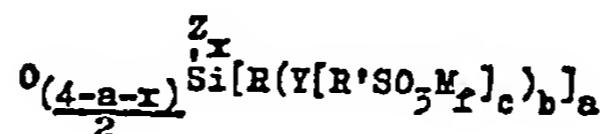
d is 0 or 1
R' is an alkylene radical that separates *Y* and SO_3 by three carbon atoms,
M is a hydrogen atom or an ammonium radical or a metal atom,
e is 1, 2 or 3

40 c is 1, 2 or 3,
 b is 1 or 2
 a is 1 or 2

a is 1 or 2
f is the reciprocal of the valency of *M*,
Z is a hydrogen atom or a monovalent hydrocarbon, halohydrocarbon, alkoxy, β -

45 α is a hydrogen atom or a halogenoalkyl, haloalkyl, alkoxy, β -alkoxyalkoxy, phenoxy, acyloxy, or hydrocarbyl-substituted isocyanoxy radical, and ϵ is 2 or 3, the sum of $\epsilon + \alpha$ being 4.

2. A siloxane having at least one unit of the general formula



where

5 R is a divalent or trivalent hydrocarbon, halohydrocarbon, or hydrocarbon ether radical, there being not more than 2 Y groups on one carbon atom, 5

Y is a $\text{C}=\text{O}$ —, —S—, —O—, $\text{C}=\text{N}$ —, $-\text{SO}_2-$, $-\text{SO}_2\text{N}-$, $-\text{N}-$, or

$\text{N}^{(\text{R}'')_d} \text{Q} \text{N}^{(\text{R}'')_d}$ radical where each

10 R'' is independently selected from the hydrogen atom and aliphatic hydrocarbon radicals containing 1 to 6 inclusive carbon atoms, 10

Q is an alkylene radical, containing 2 to 4 inclusive carbon atoms that separates the two N groups by at least two carbon atoms, and

d is 0 or 1,

R' is an alkylene radical that separates Y and SO, by three carbon atoms,

M is a hydrogen atom, an ammonium radical or a metal atom, 15

c is 1, 2 or 3,

b is 1 or 2,

a is 1 or 2,

f is the reciprocal of the valency of M,

20 Z is a hydrogen atom or a monovalent hydrocarbon, halohydrocarbon, or an alkoxy, β -alkoxyalkoxy, phenoxy, acyloxy, or hydrocarbyl-substituted isocyanoxy radical, and

x is 0, 1 or 2, any other units in the siloxane being of the general formula

$\text{A}_z\text{SiO}_{\frac{(4-g)}{2}}$ where

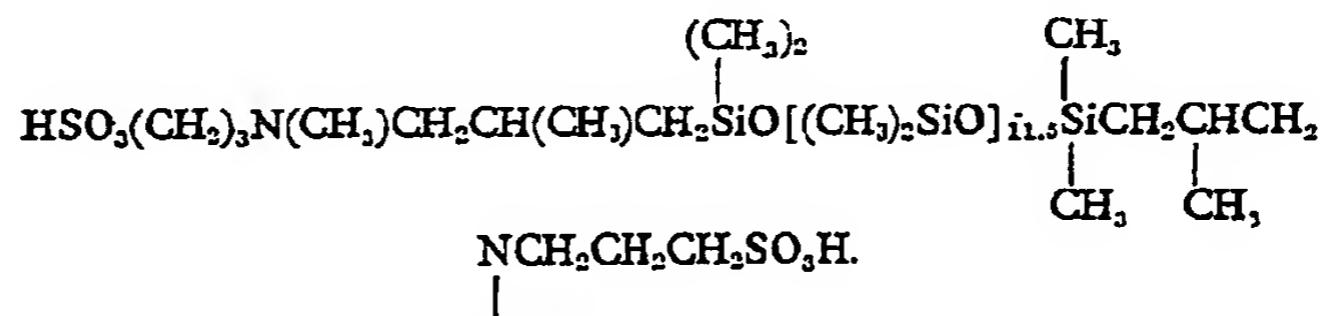
g is 0, 1, 2 or 3, and

25 A is a hydrogen atom, or a monovalent hydrocarbon or halohydrocarbon radical, or an alkoxy, β -alkoxyalkoxy, acyloxy, phenoxy, hydrocarbyl-substituted isocyanoxy, or hydroxy radical.

3. A silane of the formula $(\text{CH}_2\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2)_2\text{SO}_3\text{H}$



4. A siloxane of the average formula:



30 5. A silane as claimed in claim 1 where Y is $-\text{NCH}_2\text{CH}_2\text{N}-$.



6. A siloxane as claimed in claim 2 where Y is $-\text{NCH}_2\text{CH}_2\text{N}-$.



7. A silane as claimed in claim 1 where Y is —N—
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{—N—} \end{array}$$

8. A siloxane as claimed in claim 2 where Y is —N—
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{—N—} \end{array}$$

ELKINGTON AND FIFE,
Chartered Patent Agents,
High Holborn House, 52—54, High Holborn, London, W.C.1.,
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press
(Leamington) Ltd.—1966. Published by The Patent Office, 25 Southampton Buildings,
London, W.C.2, from which copies may be obtained.